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13. SUPPLEMENTARY NOTES					
14. ABSTRACT This research involved four projects centered on the design of theoretical and computational approaches to predict promising energetic materials and to guide the efficient synthesis of these materials. First, mixed quantum/classical methodology was developed for the simulation of photochemical reactions, which could play an important role in the design and synthesis of energetic materials. Second, the time-dependent self-consistent-field reaction path Hamiltonian method was developed for the calculation of the real-time quantum dynamics of polyatomic reactions. Third, a new approach for investigating the solvent effects of fundamental organic reactions was developed in order to aid in the efficient synthesis of energetic materials. This approach combined electronic structure calculations with reactive flux molecular dynamics calculations based on a reaction path Hamiltonian. Application of this approach to two fundamental organic reactions provided insight into the dynamical role of solvent and elucidated possible reaction mechanisms. Fourth, the Fourier grid Hamiltonian multiconfigurational self-consistent-field and partial multidimensional grid generation methods were developed for the efficient calculation of multidimensional hydrogen vibrational wavefunctions. These two methods enable the simulation of hydrogen transfer reactions required for the synthesis of polyhedral oligomeric silsesquioxanes, which are used in coatings that are resistant to extreme conditions such as heat and abrasion.					
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# Simulation of Reaction Dynamics: Nonadiabatic and Solvation Effects

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## I. Introduction

The research supported by this grant centered on the design of theoretical and computational approaches to predict promising High Energy Density Matter (HEDM) and to guide the efficient synthesis of these materials. The first objective was to develop methodology for the simulation of photochemical (i.e., electronically excited) reactions, which could play an important role in the design and synthesis of HEDM. The second objective was to develop methodology for quantum dynamical calculations of polyatomic reactions to aid in the prediction and synthesis of new energetic materials. The third objective was to investigate the solvent effects for fundamental organic reactions to aid in the efficient synthesis of HEDM. The fourth objective was to develop methodology for the calculation of hydrogen vibrational wavefunctions to enable the simulation of hydrogen transfer reactions required for the synthesis of polyhedral oligomeric silsesquioxanes (POSS), which are used in coatings that are resistant to extreme conditions such as heat and abrasion.

## II. Methods and Results

### *A. Simulation of electronically excited reactions*

We have developed new methodology for the simulation of photoexcited reactions. In these reactions, absorbed light promotes the system to a highly reactive electronically excited state, typically leading to products of higher energy than the reactants. Thus, photochemical reactions could play an important role in the design and synthesis of HEDM. One example is the photochemical ring closure of a polycyclic dialkene with two double bonds that react to produce a highly strained cage molecule such as cubane ( $C_6H_8$ ), which is a promising HEDM candidate. The ability to theoretically study the dynamics of photochemical reactions under a range of experimental conditions will help guide the efficient synthesis of promising HEDM candidates.

The simulation of photoexcited reactions is challenging since multiple coupled electronic states are involved. Thus, nonadiabatic quantum mechanical effects must be incorporated into the simulations. Fully quantum mechanical simulations are impractical for systems containing more than a few atoms. As a result, mixed quantum/classical methods have been developed for the simulation of larger systems. For photoexcited reactions, typically the quantum subsystem consists of the electrons, and the classical subsystem consists of the nuclei. One particularly successful approach for simulating photoexcited reactions is trajectory surface hopping. Our research has

focused on the Molecular Dynamics with Quantum Transitions (MDQT) surface hopping method.<sup>1-3</sup> In MDQT the classical subsystem is approximated as an ensemble of independent trajectories, and each trajectory moves classically on a single potential energy surface with the possibility of instantaneous transitions among the surfaces. The quantum amplitudes for all surfaces are propagated coherently along each independent trajectory, and the probability of a transition depends on the rate of change of the quantum probabilities determined from the quantum amplitudes. The number of transitions is minimized by specifying that the flux of trajectories switching from one state to another is uni-directional over a specified time interval. This algorithm is designed to ensure that the fraction of trajectories on each surface is equivalent to the corresponding average quantum probability. As has been noticed in the literature, however, this internal consistency is not always maintained.

The specific aim of this project was to identify the reasons for this discrepancy and to develop methods for improving the internal consistency of MDQT. We have identified two reasons for the internal inconsistency in trajectory surface hopping methods. These reasons are the existence of classically forbidden transitions and the divergence of the independent trajectories. We have developed a modified MDQT method that improves the internal consistency.<sup>4</sup> In this method, the classically forbidden transitions are eliminated by setting the nonadiabatic coupling between each pair of states to zero for the integration of the time-dependent Schrödinger equation if the corresponding transition would be classically forbidden. This approach eliminates the classically forbidden transitions since the probability of a quantum transition between two states vanishes if the nonadiabatic coupling between the two states is zero. (Note that this procedure completely avoids the controversial issue of velocity rescaling after a classically forbidden transition.) In addition to this modification, the difficulties due to divergent trajectories are alleviated by removing the coherence of the quantum amplitudes when each trajectory leaves a nonadiabatic coupling region.

We have compared the standard and modified MDQT methods to fully quantum calculations for a classic model for ultrafast electronic relaxation (i.e., a two-state three-mode model of the conically intersecting  $S_1$  and  $S_2$  excited states of pyrazine).<sup>4</sup> While the standard MDQT calculations exhibit significant discrepancies between the fraction of trajectories in each state and the corresponding average quantum probability, the modified MDQT method leads to remarkable internal consistency for this model system. For this model, the divergence of trajectories is mainly responsible for internal consistency, but the elimination of the classically forbidden transitions also leads to a minor improvement. This methodology will be useful for the simulation of photoexcited reactions aimed at the synthesis of promising HEDM candidates.

### *B. Development of TDSCF-RPH methodology*

We have developed new methodology that allows quantum dynamical calculations of general polyatomic reactions. This methodology will aid in the prediction and synthesis of new energetic materials. We developed the TDSCF-RPH (time-dependent self-consistent-field reaction path Hamiltonian) dynamics method, which allows the calculation of the real-time quantum dynamics of chemical reactions involving polyatomic molecules.<sup>5-7</sup> This approach is based on a reaction path Hamiltonian (RPH),

which characterizes the reaction dynamics in terms of motion along a reaction path and vibrational motion orthogonal to this reaction path. In this approach the reaction is assumed to occur within a multidimensional harmonic valley about the reaction path. The main advantage of such RPHs is that they require only a relatively small number of *ab initio* calculations of the potential energy surface.

Reaction path Hamiltonians have been derived for different types of reaction paths. Typically the reaction path is assumed to be the minimum energy path (MEP), which is defined as the path of steepest descent in mass-weighted coordinates starting from a transition state down toward reactants and toward products. Miller, Handy, and Adams derived a RPH that describes the reaction dynamics of a polyatomic system in terms of motion along the MEP and vibrational motion orthogonal to the MEP. This MEP RPH has been discussed extensively in the literature and has been used to describe a variety of chemical processes. Although highly successful in many areas, this MEP RPH does not provide an appropriate description of the reaction dynamics for situations in which the reaction path is sharply curved since, in this case, the dynamical motion deviates far from the MEP. To account for such situations, Miller and coworkers have developed a diabatic straight-line RPH that interpolates linearly between equilibrium reactant and product geometries of the molecular system.

We have developed the theory and numerical methodology for TDSCF quantum dynamics based on the reaction path scheme. Our first TDSCF-RPH method was based on the MEP RPH of Miller, Handy, and Adams. We derived the TDSCF equations of motion for cases in which the MEP has zero or small reaction path curvature and showed that when the coupling between the normal modes is negligible the dynamics reduces to a one-dimensional numerical time propagation.<sup>5</sup> We also numerically tested this TDSCF-RPH methodology by comparison to exact quantum dynamics based on the exact Hamiltonian for a series of simple model systems.<sup>6</sup> The success of this methodology for these simple model systems is encouraging.

Our second TDSCF-RPH method was based on diabatic RPHs.<sup>7</sup> The diabatic representation of the RPH involves a transformation of variables that shifts the coupling between the vibrational modes from the kinetic energy to the potential energy. The methodology we developed is applicable to the MEP RPH for the case in which the MEP has negligible curvature and to the straight-line RPH for the case in which the MEP has large curvature but the system follows a straight-line path instead of the MEP. We derived the equations of motion for diabatic RPHs and showed that in the diabatic representation the TDSCF dynamics reduces to a one-dimensional numerical time propagation, even for the case of large coupling between the normal modes. These numerically efficient approaches for simulating polyatomic reactions will aid in the prediction and synthesis of HEDM.

### *C. Solvent effects on organic reactions*

We have investigated the solvent effects for fundamental organic reactions. The two reactions we have studied are the Claisen rearrangement of allyl vinyl ether and the Diels Alder reaction of cyclopentadiene with methyl vinyl ketone.<sup>8</sup> Both of these reactions are useful in synthesis, so elucidation of solvent effects could aid in the efficient synthesis of HEDM. The methodology developed is also applicable to other reactions.

The reaction rates of both Claisen rearrangements and Diels Alder reactions have been found to be accelerated in polar solvents. Experimental data suggest that the Claisen rearrangement of allyl vinyl ether is accelerated by as much as a factor of 1000 in water relative to the gas phase. Moreover, experiments also indicate that the Diels Alder reaction of cyclopentadiene with methyl vinyl ketone is accelerated by a factor of 730 in water relative to isooctane.

Both the Claisen rearrangement of allyl vinyl ether and the Diels Alder reaction of cyclopentadiene with methyl vinyl ketone have been studied with a wide range of computational methods. One approach has been to perform electronic structure calculations on the reacting system in the presence of a dielectric continuum solvent. Typically these calculations are problematic due to the lack of consideration of explicit hydrogen bonding interactions. An alternative approach has been to perform Monte Carlo or molecular dynamics simulations for the reacting system in a periodic box containing hundreds of explicit solvent molecules. These calculations have been successful in reproducing experimentally measured free energies of solvation. These calculations are extremely computationally intensive, however, and most studies neglect the dynamical solvent effects. (One notable exception is the study by Voth and coworkers, which includes a reactive flux calculation of the dynamical transmission coefficient.)

We have investigated the solvent effects for these two reactions within the framework of the reaction path Hamiltonian (RPH) developed by Miller, Handy, and Adams.<sup>8</sup> This RPH is based on the minimum energy path (MEP) described above. The initial step of this project was the generation of the MEPs at the DFT/B3LYP/6-31G\* level for these reactions in the gas phase and in the presence of two explicit water molecules. We found that the presence of the two water molecules lowered the activation energy barrier due to stronger hydrogen bonding between the water molecules and the solute oxygen in the transition state than in the reactant. The magnitude of the calculated free energy of solvation agreed qualitatively with experimental estimates and other calculations. We also analyzed the geometries and partial charges along the MEPs to determine the structural and electrostatic roles of the water molecules. In both cases we found that the presence of the water molecules resulted in a looser, more dissociative transition state. We also found that the transition state was more polar in the presence of the water molecules.

In addition, we analyzed the frequencies, couplings, and curvatures along the MEPs in terms of the RPH for the two reactions in the gas phase and in the presence of two water molecules.<sup>8</sup> The Claisen rearrangement exhibits a curvature peak on the reactant and the product side, but the Diels Alder reaction exhibits only a peak on the product side. For both reactions, the overall curvature increases in the presence of the two water molecules due to coupling of the solvent to the reaction coordinate. The strongly coupled modes in the gas phase contain contributions from the stretching motion of bonds that are broken and formed during the reaction. In the presence of two water molecules, the strongly coupled modes contain additional contributions from the stretching motion of the hydrogen bonds between the water molecules and the solute oxygen. We found that the solvation increases the curvature more for the Diels Alder reaction than for the Claisen rearrangement, indicating that the water molecules are more strongly coupled to the reaction coordinate for the Diels Alder reaction.

We have calculated the dynamical transmission coefficients for both reactions using reactive flux molecular dynamics methods based on a reaction path Hamiltonian.<sup>8</sup> Due to the locations of the coupling peaks, reflections occur in both the reactant and the product regions for the Claisen rearrangement but only in the product region for the Diels Alder reaction. (For both reactions, reflections may also occur in the transition state region.) Recrossings of the transition state in the forward direction were observed for the Diels Alder reaction but not for the Claisen rearrangement. The transmission coefficients were nearly unity for the Claisen rearrangement both in the gas phase and in the presence of two water molecules. In contrast, the transmission coefficients were slightly smaller for the Diels Alder reaction:  $\kappa=0.95$  in the gas phase and  $\kappa=0.89$  in the presence of two water molecules. The smaller transmission coefficients for the Diels Alder reactions are due mainly to the flatter potential energy along the reaction coordinate near the transition state and the closer proximity of the coupling peak to the transition state. These differences lead to lower momentum along the reaction coordinate in the strong coupling region and thus a higher probability of reflections. The decrease in the transmission coefficient for the Diels Alder reaction in the presence of two water molecules is due to a combination of a flatter potential energy along the reaction coordinate near the transition state and a larger curvature peak on the product side.

Our investigation of the solvent effects for these two fundamental organic reactions elucidated the electrostatic, structural, and dynamical roles of water molecules, as well as possible reaction mechanisms. This approach is less computationally intensive than full-scale molecular dynamics simulations but still provides useful qualitative information about dynamical solvent effects. Moreover, this general approach can be used to study the effects of different solvents. This type of comparative study will be useful for the efficient synthesis of HEDM candidates.

#### *D. Calculation of hydrogen vibrational wavefunctions*

We have developed new methodology for the calculation of hydrogen vibrational wavefunctions for systems in which only one or a few specified hydrogen atoms are treated quantum mechanically, and the remaining nuclei remain fixed.<sup>9-11</sup> This methodology will enable the simulation of hydrogen transfer reactions required for the synthesis of polyhedral oligomeric silsesquioxanes (POSS). POSS is important to the HEDM project for use in coatings that are resistant to extreme conditions such as heat and abrasion.

The methodology we developed to calculate hydrogen vibrational wavefunctions is called the FGH-MCSCF (Fourier grid Hamiltonian multiconfigurational self-consistent-field) method.<sup>9</sup> In the FGH-MCSCF method, the potential energy surface for the transferring hydrogen(s) is calculated on a grid (i.e., all nuclei except the transferring hydrogen(s) are fixed, and the energy is calculated for the hydrogen(s) positioned at each point on the grid). The hydrogen vibrational wavefunctions are calculated by numerically solving the time-independent Schrödinger equation for the hydrogen nucleus (or nuclei) moving on this potential energy surface. The multidimensional wavefunctions are calculated with an MCSCF approach, where each hydrogen vibrational wavefunction is expressed as a linear combination of single configurations that are products of one-dimensional wavefunctions represented directly on the grid. The variational method is

utilized to minimize the total energy with respect to both the configuration coefficients and the one-dimensional wavefunctions. We have found that only a relatively small number of configurations are required for the calculation of accurate hydrogen vibrational wavefunctions. Thus, the FGH-MCSCF approach avoids the diagonalization of large matrices required for a full configuration interaction approach. In order to further increase the efficiency of the calculation of nuclear wavefunctions, we have developed a partial multidimensional grid generation method.<sup>11</sup> This method substantially decreases the number of potential energy calculations by avoiding this calculation for grid points with high potential energy. We have tested both the FGH-MCSCF and the partial multidimensional grid generation methods by application to hydride transfer in model systems.<sup>10,11</sup> This methodology will be useful for the investigation of hydrogen transfer reactions required for the synthesis of POSS.

### III. Summary

Thus, we have achieved the four research objectives listed in the Introduction. First, we further developed the Molecular Dynamics with Quantum Transitions (MDQT) surface hopping method for the simulation of electronically excited reactions. The internal consistency of MDQT was improved by eliminating classically forbidden transitions and by damping the coherence of the quantum amplitudes. Second, we developed the TDSCF-RPH (time-dependent self-consistent-field reaction path Hamiltonian) dynamics method for the calculation of the real-time quantum dynamics of chemical reactions involving polyatomic reactions. In addition to the development of the theory and computational algorithm for TDSCF-RPH, numerical tests were performed on model systems. Third, we investigated the solvent effects for a Claisen rearrangement and a Diels Alder reaction. Our approach combined electronic structure calculations with reactive flux molecular dynamics calculations based on a reaction path Hamiltonian. Analysis of the dynamical trajectories provided insight into the dynamical role of the water molecules and elucidated possible reaction mechanisms. Fourth, we developed the FGH-MCSCF (Fourier grid Hamiltonian multiconfigurational self-consistent-field) and partial multidimensional grid generation methods for the efficient calculation of multidimensional hydrogen vibrational wavefunctions. These two methods were applied to hydride transfer in a model system. All of these new theoretical and computational approaches will aid in the efforts of the Air Force to predict promising energetic materials and to guide the efficient synthesis of these materials.

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